Glass and Ceramics, Vol. 69, Nos. 1 – 2, May, 2012 (Russian Original, Nos. 1 – 2, January – February, 2012)

EFFICIENCY AND QUALITY

UDC 666.1

RAW MATERIALS WITH PRESCRIBED PROPERTIES — ADDITIONAL RESOURCES FOR INCREASING GLASS-FURNACE EFFICIENCY AND FLOAT-GLASS QUALITY

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Translated from *Steklo i Keramika*, No. 1, pp. 3 – 8, January, 2012.

The results of a study of the quality variability of float-glass produced with top-grade equipment and technology are presented and the reasons for the fluctuations are analyzed. It is concluded on the basis of the analysis that consistently high-quality product cannot be obtained without increasing the quality of the raw materials used for making batch. In our opinion, the best way to solve this problem is to tighten the specifications for the raw-materials components used for glass batch and to set high, firmly established quality specifications.

Key words: glassmaking, raw materials, technological specifications, batch, glass quality.

The large changes which have occurred in the market for glass products, especially sheet glass, concern first and foremost high product quality. The following are now the principal parameters used for quality evaluation:

– high optical indices;

– high light transmission (transparency), more than 90%;

– cut quality, including the condition of the glass edge and good (soft) cutting on glass cutting tables during subsequent industrial processing of the glass;

– large-format glass dimensions, to 6000 mm and larger;

– no defects of any kind visible to the unaided eye on glass sheets.

At the same time, in Russia substantial retooling of the glass industry, especially for sheet-glass production, has occurred recently. Modern, completely automated float-glass lines have been built. Glass furnaces operate with high specific throughput of molten glass and low heat consumption for the process; these furnaces meet present-day requirements and are equipped with automatic monitoring and control of the main glassmaking parameters.

Conventionally, all problems arising in glass making, forming, and annealing are due to batch quality. At Salavatsteklo JSC the batch preparation process has been modernized. New, modern technology using equipment manufactured domestically (Stromizmeritel’ JSC, Novgorod) and in the West (the firms Zippe, Emmaglass, and others) has been introduced.

However, even with such top-notch equipment and technologies for float-glass production it is impossible to achieve consistent production of high-quality product if the problems of increasing the quality of the raw materials used for the production of the glass batch are not solved.

On the basis of what has been reported at Salavatsteklo JSC it is now believed that the most effective way to improve product quality is to use for glass-batch production better raw materials with prescribed quality specifications. This will also become an additional resource for increasing glass-furnace efficiency, which, in turn, will enable consistent production of high-quality product.

A systems analysis of the operation of float-glass lines (specifically, evaluation of the stability of the glassmaking process and the production of high-quality product as a function of the quality of the raw materials) performed at Salavatsteklo confirms that such a change in the ideology and approaches to quality specifications for raw materials is correct. The principal question concerns the more exacting quality specifications, both standard and technological, for raw materials which suppliers must take into account.

Definite advances have already been made regarding raw-materials quality and transport. In this connection, it must be underscored that the content of impurities, especially

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iron, in a number of materials has decreased sharply, enriched-sand delivery has improved, most enterprises have switched to heavy soda, and revolving doors have been developed for open wagons and hoppers, which has made it possible to completely prevent chromites from entering batch or to decrease their amount in batch. However, as before, the quality of the raw materials obtained from different suppliers differs considerably. Often, the chemical composition of the raw materials obtained from the same supplier fluctuates from one batch to another.

In Western Europe and the USA, raw materials must meet stringent technical specifications. For example, a special commission of the German Technical Glass Society DGG has formulated informational sheets for raw-materials. These sheets consist of tables of the principal raw materials required for glass-batch preparation [1]. These tables contain, together with data on the chemical composition and particle-size distribution, a general description of the raw materials and information about their mineralogical and geological properties. Considerable attention is devoted to the granulometric structure of each type of raw material having a large effect on the mixing of the batch components and batch separation and melting as well as on the rate of glass formation and fining. Ultimately, the raw materials used largely determine both the product quality and the service life of a glass furnace.

In Russia, the currently operative state standards (GOSTs) and technical specifications for raw materials are less stringent and largely conform to the technical capabilities of the raw-materials suppliers.

Any discussion of the quality of the raw materials used for the preparation of glass batch must start with quartz sand — the principal component of the batch, whose chemical and physical properties are decisive for obtaining a high-quality finished product. The chemical and granulometric compositions of sand from different deposits (quarries) differ somewhat from one deposit to another. Sand quality is determined by, first and foremost, the geography of the deposit as well as the methods used for extraction and processing.

The Eganovskoe (Moscow Oblast, Ramenskoe Mining and Enrichment Combine) and Tashlinskoe (Ul'yanovsk Oblast, Tashlinskii Mining and Enrichment Combine) deposits have the best quartz sand for float-glass production. Quartz sands from promising (in our opinion) deposits Muraevnya (Ryazan Oblast) and Zykovskoe (Orenburg Oblast) have come into use relatively recently for the production of float-glass. In the long term, quartz sands produced by Koktas-Aktobe JSC (Republic of Kazakhstan) must be considered for extensive use in the production of float-glass in Russia.

To produce high-quality float-glass, special attention must be given to the problem of decreasing to a minimum the content of elements often encountered in the quartz sands, such as Fe, Cr, Al, Ti, Zn, Mg, Mn, and Ca. The presence of the coloring ions of chromium and manganese is especially undesirable in sand.

The most important technological properties of quartz sand used in glass production are the content of iron oxides and the granulometric composition of the sand.

Iron oxides actively participate in redox processes during glassmaking. The Fe^{2+} oxide formed in the process lowers the diathermancy of the molten glass, which changes the temperature regime of glassmaking considerably and degrades product quality. Low iron corresponds to high diathermancy of the molten glass. The principal effects of low iron are higher temperature at the bottom of the furnace and stronger circulation of the molten glass. For low molten-glass viscosity at the furnace bottom the glass flow regimes in the melting zone can react to very small changes of the conditions in the furnace [2]. In this connection, the following must be taken into account in order to control the technological processes of glassmaking:

– the molten-glass temperature at the bottom:
  - at the melting tank bottom beneath the batch;
  - at the end of the melting zone in front of the waist;
  - at the end of the conditioning area of the furnace;
– the depth of the cooler barrier in the waist area;
– the operation of the molten-glass stirrers installed in the waist area after the cooler barrier;
– the ratio of the iron oxides according to the RedOx value (daily check).

The studies performed at Salavatsteklo showed that the best quality obtains with 0.03 – 0.04%[3] Fe_2O_3 in the sand. However, the Fe_2O_3 content of quartz sand batches delivered to the plant varies from batch to batch in the range 0.03 – 0.06%. This makes it more difficult to maintain a stable glassmaking regime and leads to all the attendant negative consequences.

Studies of the grains of unenriched sand have revealed that clayey impurities in the form of an alumina film and alumina filling cracks present on the surface of the sand grains stick to the surface of the grains. It is well known that after being mixed with glass-batch components and wetted with water the soda coats the sand grains and accelerates their melting when the molten glass is made. However, the alumina film weakens this contact and thereby slows down glass formation.

According to the data in [1], quartz sand consisting of about 95% particles with sizes 0.1 – 0.4 mm has proven to be very good for producing sheet glass. However, the presence of quartz particles with diameter > 0.5 mm in the sand lowers the rate of glass formation during the glassmaking process. This creates technologically clearly expressed prerequisites for lowering the molten-glass capacity of the furnace or the formation of defects in the form of batch stone as well as silica foam, which results in high rejection of glass (mainly, cristobalite inclusions) (Fig. 1).

A quantitative estimate made of the degree of melting quartz grains as a function of their size (i.e., the glass formation time) on the basis of the data in [3] confirms convin-

[3] Here and below, the content by weight.

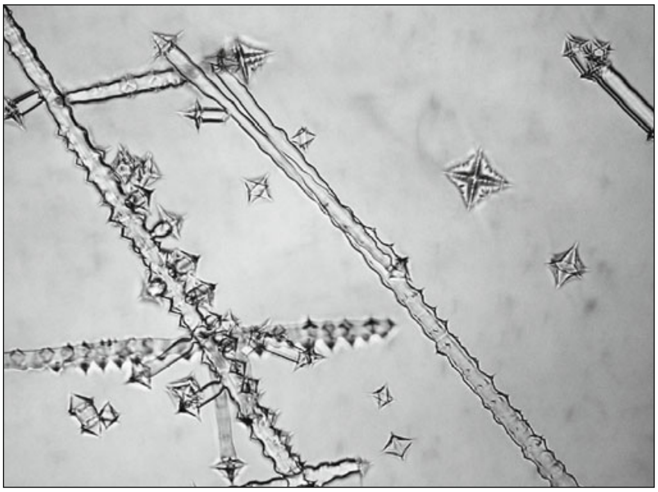

Fig. 1. Transmitted light photograph of cristobalite crystals in float-glass taken from a float-glass line at the Salavat plant. ×100; the crystals range in size from 32.3 to 389.5 μm.

cingly that it is technologically sound to use in float-glass production quartz sand whose main fraction consists of about 95% 0.1 – 0.4 mm in diameter grains.

For example, the melting time of 0.5 mm grains of quartz sand is 2 and 3.5 times longer than that of 0.4 and 0.4 mm in diameter grains, respectively. And the melting time of 0.3 mm in diameter quartz grains is approximately 1.5 times shorter than that of 0.4 mm in diameter grains.

Undoubtedly, the next progressive step to further improve the capacity of float-glass furnaces is to switch to quartz sand whose principal fraction consists of 80 – 85% 0.1 – 0.3 mm in diameter grains and approximately 10 – 15% 0.4 mm in diameter grains.

The present authors have analyzed the standards in effect in the USA, China, and Germany compared with those in use at the Salavat and Saratov plants. They have found that 0.8 – 0.5 mm sand grains are not permissible in glass production. Sands with 0.4 – 0.1 mm grains comprise 95 – 97%, the 0.3 – 0.1 mm fraction comprising 80% of which 0.1 mm grains comprise no more than 7.0%, and .1 mm grains are not permitted (screening onto a bottom pan).

Together with the particle size, the specific surface area of the sand particles also greatly affects the character of the melting of the sand. Here, it should be kept in mind that cracks present on the surface of grains increase the specific surface area of the sand particles. When sands are enriched and dried in drums the initial 0.4 – 0.1 mm sand particles acquire new surface qualities after leaving the drying drums — needle and rounded shapes with an extended crack-covered surface. Analysis has shown that after sand is enriched there is virtually no sticking of clayey impurities in the form of a film on the surface of the grains and in cracks (Fig. 2).

In summary, enriched sands with grains heat-treated during drying, iron content 0.04 – 0.03%, and particle size 0.4 – 0.1 mm have an advantage over other sands and stabilize the glassmaking process.

Fig. 2. Transmitted light photographs of quartz-sand grains, ×100: *1*) Tashlinskii Mining and Enrichment Combine (Tashlinskii MEC) enriched sand, grain size about 430 μm; clean, smooth surface, practically no sticking of clayey impurities on quartz grains, surface and deep cracks present; *2*) Luk’yanovskii MEC sand) unenriched, grain size about 350 μm; rounded surface but with clearly defined facets, fine and surface cracks, clayey impurities sticking to quartz grains; *3*) Luk’yanovskii MEC sand after processing at the Salavat plant, grain size about 340 μm; rounded surface, fine surface cracks, coarser cracks are seen in single-digit numbers, very little sticking of clayey impurities in the form of films on quartz grains.

The principal source of alkali raw material is soda ash, which is used to introduce up to 14% sodium oxide into the glass composition. Primarily two forms of soda are used in the production of glass — heavy and light. At the present time, heavy soda is used in all float-glass plants. The main suppliers of this soda are Soda JSC (Sterlitamak) and the Bereznikovskii Soda Works. Heavy soda in the form of granules is used in batch production; its advantages over light soda are high content of the principal material Na_2CO_3, bulk density 900 – 1100 kg/m^3 instead of 630 kg/m^3, 20°C lower

melting temperature (830°C), and larger particles (granules) 0.2 – 1.2 mm.

The granulometric composition of the soda is important for obtaining a uniform batch and activating glassmaking processes. Soda with particles smaller than 0.1 mm degrades the batch preparation process; this is because when moisture enters the batch during the wetting operation the soda clumps and batch uniformity decreases. Increased loss of light soda already occurs as the batch is transported from the doghouse to the glass furnace and loaded into the furnace as well within the furnace itself.

Measurements were performed on the float-glass furnaces in the Salavat plant and the soda loss was determined. The loss exceeded 35% of the total loss of the raw-materials components in the first two pairs of regenerators and up to 30% in four pairs of regenerators.

The objective is to remove from the soda the fine fraction with particle size < 0.1 mm so as to prevent dust generation during transport and loading into the glass furnace, prevent batch separation and losses, and obtain a soda fraction with particle size ≥ 0.5 mm.

P. Émmer established that when heavy soda is used the initial indications of batch separation appear when the soda particles are smaller than the sand grains [1]. Close contact of 0.5 mm and larger heavy-soda particles with the other raw materials in the batch improves moisture retention, increases the reactive surface area of the batch, prevents batch separation, promotes a high degree of uniformity, and shortens the melting time of the sand grains during the glassmaking process.

An important soda quality indicator is the absence of undesirable impurities, first and foremost, NaCl. Up to 0.5% NaCl is permitted in top-quality soda, which degrades the service life of glass furnaces. Up to 0.2% NaCl is permitted in the best soda. Lowering the NaCl content in soda from 0.5 to 0.2 – 0.1% is an important objective of soda combines.

In summary, to improve batch quality and increase the efficiency of glass furnaces the content of the main material Na_2CO_3 in heavy soda must be at least 99.5%, the granulometric particle composition must be 0.5 – 1.0 mm with no more than 5.0% residue of particles smaller than 0.1 mm in the bottom pan, and the NaCl content must not exceed 0.1 – 0.2%.

Of course, quartz sand and soda are considered to be the principal raw materials, even taking account of the volumes used, in the production of float glass. At the same time, carbonate raw materials — dolomite and limestone — have an important place in the production of batch for making float glass. In the domestic glass industry, there are many quantity and quality problems in obtaining such raw materials.

It should be noted that in the past the glass industry in Russia and the Commonwealth of Independent states obtained carbonate raw materials in the form of chunks, which were immediately processed into powder (milled dolomite) at the glass works. No special significance was attached to the granulometric composition of dolomite and limestone particles. During the same period the European glass industry obtained for the production of batch ready-made concentrate in the form of milled dolomite with strictly prescribed quality characteristics of the raw material.

As modern float- and container-glass lines were built in domestic glass plants a considerable demand arose for ready-made concentrate of milled carbonate raw material.

At the present time "NPP Izvestnyaki i dolomity" JSC (Andreevka, Vladimir Oblast) and the Kovrov dolomite quarry (Kartaly quarry in Chelyabinsk Oblast) produce flour-like dolomite. However, the materials supplied by these enterprises do not meet the modern quality specifications with respect to the granulometric composition and iron oxides content. In addition, these enterprises cannot supply the required volume needed by the glass industry in Russia.

Dolomite gravel is produced in the town of Krasnousol'skii in Bashkortostan. This gravel is used at the Salavat plant to make milled dolomite.

It is important that carbonate raw material have definite properties, such as the admissible particle-size range and the moisture and iron contents. For the technological requirements of the glassmaking making process and the conditions for preparing batch, the main problem is to produce materials consisting mainly of particles ranging in size from 0.5 to 2.0 mm but with the content of the fine fraction not exceeding 5 – 10%. It has been determined that if the particles are smaller than 0.1 mm, considerable dust is generated. Likewise, separation occurs when the dolomite material is too fine. Studies of the rates of reactions occurring during glassmaking show that batch melting is greatly accelerated if the dolomite particles range in size from 0.2 to 1.0 mm. In addition, quartz dissolution is intensified.

To increase the quality of milled dolomite it is necessary to modernize the equipment and, possibly, the technology used at the production plants. Most importantly, the milling and sieving equipment must be replaced. This will make it possible to obtain milled dolomite with a prescribed granulometric composition and to sharply decrease the content of equipment iron in the raw material.

Of course, additional financing is required, but it will pay for itself.

The milled dolomite produced at the Salavat plant using dolomite gravel from the Krasnousol'skii quarry does not meet the specifications for float-glass production mainly with respect to the granulometric composition. However, even milled dolomite purchased elsewhere will not secure the required quality and quantity of this material.

This problem is even more acute for limestone. Natural, good-quality limestone exists in many regions. However, the production of limestone milled from natural limestone has not been organized. Each plant solves this problem independently. Modern float-glass plants have largely switched to synthetic chalk, which contains large amounts of iron — from 0.2 to 0.5%, the granulometric composition of 0.1 – 0.5 mm particles is greater than 50%, and particles smaller

TABLE 1. Specifications for Quality of Raw Materials for Float-Glass Production

Raw material	Main material content, wt.%	Harmful impurity content, wt.%					Particle-size composition	
		Fe_2O_3	NaCl	Cr_2O_3	ZrO_2	TiO_2	Fraction, mm	Content, %
Quartz sand	≥ 99.5	0.03 – 0.04	Absent	Absent	Absent	0.01 – 0.02	0.1 – 0.4 0.4 – 0.5 < 0.1	95 ≤ 3.0 ≤ 1.0
Heavy (granular) technical, calcined soda	≥ 99.0	≤ 0.005	≤ 0.2	Absent	Absent	Absent	0.5 – 1.0 < 0.1	90 ≤ 10.0
Dolomite	MgO ≥ 18.0 CaO ≤ 34.0	≤ 0.25	Absent	Absent	Absent	Absent	0.2 – 1.0 < 0.5	95 ≤ 5.0
Sodium sulfate	Na_2SO_4 ≥ 98.0	≤ 0.015	≤ 0.2	Absent	Absent	Absent	0.5 – 2.0 0.1 – 0.5	≥ 99 ≤ 1
Limestone (chalk)	Calcium, magnesium, and strontium carbonates (in terms of calcium carbonate) content ≥ 93.0	≤ 0.1	Absent	Absent	Absent	Absent	0.5 – 2.0 < 0.1	≥ 90 ≤ 10
Feldspar	Al_2O_3 ≥ 21.0	≤ 0.2	Absent	Absent	Absent	Absent	0.5 – 1.0 0.4 – 0.5 0.1 – 0.4 < 0.1	1 2 85 ≤ 5.0
Carbon (CCM*)	≥ 91	Absent	Absent	Absent	Absent	Absent	> 1.0 0.63 – 1.0 0.1 – 0.63 < 0.1	20 15 60 ≤ 5

* CCM) Carbon-containing material.

than 0.1 mm comprise 15% (bottom pan residue). At the Salavat plant this chalk degraded glassmaking and increased energy consumption.

It should be noted that because natural limestone has many technological advantages float-glass manufacturers in the West use only natural limestone. For example, limestone shellrock is used in Germany [1].

The granulometric composition of milled limestone is approximately the same as that of milled dolomite.

In summary, to obtain high-quality carbonate material its iron content must be decreased to 0.05 – 0.1% and to obtain the required granulometric composition the content of 0.5 – 2.0 mm particles must be 90 – 95% and that of < 0.5 mm particles must be 5 – 10% (residue on bottom pan).

The most important raw material for introducing alumina into glass is feldspar. Once again the determining factors here are the granulometric composition of the raw material and the iron oxide content. One of the best feldspar deposits in Russia is considered to be the Vishnevogorskoe deposit. However, the iron oxide content of this feldspar fluctuates strongly — from 0.25% to 0.4%, indicating fluctuations from one delivery to another. The granulometric composition of the feldspar particles likewise fluctuates. Particles of size 0.6 – 0.4 mm comprise 15 – 20%, 0.4 – 0.1 mm 60 – 70%, and < 0.1 mm 5.0 – 15%.

At the Salavat plant magnetic separators were installed in the process line of this material to improve the quality of feldspar. This made it possible to decrease the iron content in the feldspar from 0.35 to 0.25% (about 30%).

Thus, feldspar suppliers must adopt measures to lower the iron content of their feldspar to 0.1 – 0.2%. In addition, the content of 0.4 – 0.1 mm particles in the granulometric composition must be increased to 80 – 90%.

Mention should be made of the use of sodium sulfate and carbon in float-glass production. Sodium sulfate and carbon have become necessary batch components for making float glass, largely determining the efficiency of glassmaking processes [4].

The decisive role of sodium sulfate as a fining agent and that of carbon as a reducing agent must be underscored. They ensure normal flow of the redox processes in the molten glass and make it possible to control the diathermancy of the glass melt.

Sodium sulfate is an oxidizer. It is an effective fining agent for molten glass and accelerates the glassmaking process. Conversely, carbon is an active reducing agent in the glassmaking process.

The work performed at the Salavat plant on selecting sodium sulfate from different producers has shown that the determining factor, aside from the content of the main material,

is the granulometric composition of sodium sulfate, especially its content of powdered fractions.

The use of sodium sulfate with the optimal granulometric composition with particle sizes 0.5 – 2.0 mm (99.0%) and 0.1 – 0.5 mm (< 1%) did the following:

– considerably improved the mixing of the components during batch preparation using mixers;

– improved the melting of the glass batch in the furnace;

– increased the temperature beneath the batch layer in the furnace while decreasing the maximum melting temperature in the gas medium.

As a fining agent, sodium sulfate is introduced into the batch at the same time as carbon. The properties of carbon as a reducing agent largely depend on its form, quality, and especially content.

The possibility of using different coals in glassmaking has been studied at the Saratov Institute of Glass [5].

Coals from different suppliers were tested at the Salavat plant in its own float-glass lines.

Carbon-containing materials (CCMs) greatly improve furnace operation. The advantage of CCMs over other sorts of carbon lies mainly in their better granulometric composition. Their content of the 0.1 – 3.0 mm fraction is 87%, and the carbon content is > 90%.

In summary, the studies performed at the Salavat plant to determine the dependence of the efficiency of float-glass lines on the raw-materials quality make it possible to formulate the specifications for the quality of the raw materials used in the production of float-glass. These specifications are presented in Table 1.

Summarizing, it should be noted that because of the modern designs of glass furnaces, the adoption of automatic systems for controlling the glassmaking processes, and the use of modern equipment and new technologies for making glass, we have learned how to control these processes and have taught automatic machines how to do so. Today, automatic machines run the melting, formation, and annealing processes according to a prescribed regime. However, the system controlling the batch preparation processes must be improved.

Without solving the problems of increasing the quality of the raw materials and stabilizing the chemical and physical indicators (parameters) of the raw materials taking account of the modern requirements substantial difficulties arise in controlling batch preparation with modern technological specifications.

The use of higher-quality raw materials with stable properties will make it possible to increase the efficiency of glass furnaces considerably and to improve the quality of the final product.

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